THE EFFECT OF IMPURITIES ON ETHANE HYDRATE INDUCTION TIMES

Martin Bylov
Calsep A/S
Gl.Lundtoftevej 7, 2800 Lyngby
Denmark

Peter Rasmussen
Department of Chemical Engineering, The Technical University of Denmark
Building 229, 2800 Lyngby
Denmark

ABSTRACT
Three series of ethane hydrate formation experiments have been performed. The first series was carried out at 14 bar and 3 °C. Very scattered induction times (40,000 to 340,000 seconds) and less scattered growth rates were observed. Before the next series the cell was cleaned very thoroughly. With similar experimental conditions the induction time was longer than three weeks after which period of time the pressure was increased to 21 bar. Scattered induction times (10,000 to 150,000 seconds) and slightly higher growth rates were obtained. The third series was carried out at 20 bar and with 20 mg of impurities added. Short induction times and slightly lower growth rates were observed. All the experiments have been simulated using the hydrate kinetics model proposed by Skovborg (3). The experiments lead to the overall conclusion that impurities almost eliminate the induction time. This should be considered when transferring laboratory results to field conditions.

INTRODUCTION
The original scope of the presented experimental work was to establish an experimental procedure which would result in reproducible induction times. In the work by Skyum (1) and Andersen (2) numerous ethane hydrate experiments were carried out. Between each experiment the cell was opened, emptied and cleaned. Under seemingly identical conditions, large variations in the induction times were observed. It was assumed that a random amount of dust/dirt would be present in the cell in each experiment resulting in the observed variations in the induction times. Consequently it was decided to keep the cell closed between experiments thus having the same amount of dust/dirt in the cell throughout the measurement series.

EXPERIMENTAL SETUP AND PROCEDURE
The experimental setup is outlined in figure 1. The cell is a stainless steel container with a volume of 66.5 cm³. Sapphire windows are placed on two opposing sides. The cell is closed with a lid, through which the gas and water are lead to the cell. The pressure sensor is placed in the lid while the temperature sensor is placed in an oil filled pocket in the cell. The temperature in the cell is controlled by flowing a water/ethanol mixture through the cooling jacket. The cell is placed on top of a magnetic stirrer, that can rotate a teflon coated magnetic rod in the cell. The maximum working pressure of the cell is 60 bar.

Before the first experiment in a series, the cell is cleaned and then evacuated. The desired amount of water is introduced and the pressure is increased to the desired level using ethane gas. The cooling flow is started and gas hydrates will eventually form. When no further gas hydrate formation takes place, the cooling flow is stopped The cell with content is left for 4-5 hours to dissociate all formed hydrates and to heat up the cell to ambient temperature. The cooling flow is then restarted, and a new experiment can start.

RESULTS - SERIES 1
Before the first series the cell was cleaned in the same way as used by Skyum (1) and Andersen (2). This means rinsing with distilled water and drying using compressed air. The cell was evacuated and loaded with 20 cm³ of distilled water and ethane at 21°C. Series 1 was started with a temperature setting of 3 °C. Figure 2 shows the pressure transient and part of the temperature transient of the first experiment (M6). The pressure initially drops from 15.3 bar to 14.0 bar due to the reduction in temperature from 21 °C to 3 °C. The pressure and the temperature then remain constant until the end of the induction time. As hydrates start to form the pressure drops dramatically due to gas consumption and there is a small increase in the temperature due to the heat evolved. The course of events in experiment M6 is representative for all the experiments in series 1 and 2.

A total of 11 experiments is included in series 1 and the results are shown in table 1 and in figure 3. The induction time is here defined as the time that elapses from the cooling flow is started and until the pressure starts to drop due to hydrate formation. To calculate the amounts of hydrate formed within 600 and 3600 seconds respectively after the induction period, the computer program HYLAB

has been used. The HYLAB program is essentially based on the gas hydrate kinetics model proposed by Skovborg (3):

$$\frac{dn}{dt} = k * A * c_{w0} * (x_{int} - x_b) \tag{1}$$

dn/dt : Gas consumption rate.
k : Mass transfer coefficient.
A : Gas/water interfacial area.
c_{w0} : Molar concentration of water in the water phase.
x_{int} : Mole fraction of gas in water phase at the gas/water interface in equilibrium with the gas phase.
x_b : Mole fraction of gas in the water phase in equilibrium with the gas hydrate.

In principle the model requires knowledge of the product k*A to be able to calculate the gas consumption rate and the pressure drop with time.
When analysing experimental data as here the model is rearranged to allow a measured pressure drop to be converted into a gas consumption rate giving as the results the amount of hydrate formed and the product k*A.
The induction time varies between 38209 seconds and 341430 seconds whereas the growth rates are much more uniform.

RESULTS - SERIES 2
After discovering that simply keeping the cell closed between experiments thus keeping the composition constant did not yield reproducible induction times it was decided to try to eliminate the effect of presence of impurities. The cell was consequently cleaned much more thoroughly using only double distilled water and drying with dust free paper. Similar conditions to those used in series 1 were established. More than three weeks (~2,000,000 seconds) passed after pressurizing the cell and no hydrates were formed. The pressure was then increased to 21 bar. Approximately 38500 seconds later hydrates eventually formed. Series 2 comprises this and five more experiments at 3 °C and 21 bar. The results are shown in table 2 and in figure 3. Not surprisingly the growth rates were higher in series 2 than in series 1. The induction times were on the average lower (table 4) but still very scattered

RESULTS - SERIES 3
The results in series 1 and 2 showed that even minor amounts of impurities have some effect on the induction time. Consequently it was decided to add a large amount of impurities to the system to make it insensitive to addition of further impurities. It was decided that the "composition" of the added impurities should to some degree match the solid material found in multiphase pipelines. The impurities consist of equal amounts of $CaCO_3$, $BaSO_4$, rust and asphaltenes. Before addition of water and gas to the cell, 20 mg impurities was added and conditions similar to those of series 2 were established. The course of events in the experiments of series 3 differs drastically from that of the other experiments. In series 3 the pressure initially not only drops due to reduction in temperature but also because hydrates were formed shortly after the hydrate equilibrium temperature is reached. The observed induction time in table 3 is the time from the beginning of cooling until some hydrate particles were seen. In table 3 is also listed the time it takes before the conditions in the cell are favourable for hydrate formation from an equilibrium model (4) point of view. It can be seen that hydrates were often observed before the conditions for their formation were favourable. This cannot be contributed to low accuracy in the gas hydrate model used, but rather to the fact that there is some time delay in the temperature measurement. In all experiments performed in the cell the pressure start dropping for approximately 30 seconds before any change in the temperature is seen. For that reason it seems likely that gas hydrates start to form shortly after the actual conditions in cell are favourable for their formation.

DISCUSSION
The results in series 1 and 2 indicate that induction times are very hard to reproduce even under seemingly identical conditions. Series 3 indicates that addition of large amounts of impurities almost eliminates the induction time. It is however difficult from the present data to say whether the standard deviation on the induction times in series 3 is as large as for the other experiments. Comparison between the observed induction times in series 3 and the time after which the hydrate formation is favourable could indicate that the induction times also in this case are scattered, though very short.
The growth rates are for all series much less scattered than the induction times and thus easier to compare. It is no surprise that the growth rate in series 2 is larger than in series 1 since the driving

force for hydrate formation is considerably higher. Expressed in terms of the Skovborg model, the difference $x_{int} - x_b$ is larger in series 2 ($\sim 3.7 * 10^{-4}$) than in series 1 ($\sim 1.8 * 10^{-4}$).

When looking at the average $A * k$ which is needed to describe the experiments in series 1 and 2, it is interesting to note that a smaller value applies for series 2. One must assume that the interfacial area is the same in both series, i.e. k must differ. This observation has two possible explanations. Either the mass transfer coefficient is pressure dependent or the mass transfer of ethane from the gas phase to the water phase is not the only significant kinetic step. If for example the building up of gas hydrate crystals is also a significant kinetic step, one must assume that x_b will be higher than predicted from a gas hydrate equilibrium point of view. If x_b is in fact higher than predicted by the model, an analysis of the data assuming equilibrium between the water phase and the hydrate phase will result in a higher value of $A * k$ as it is the case in series 1 compared to series 2. This could suggest that when the driving force for hydrate formation is small, the building up of crystals is a significant step, whereas it becomes less significant for larger driving forces.

When analysing the amount of hydrate formed in series 3 it is seen that during the first 600 seconds it is even lower than the results obtained in series 1, whereas at later times the results are comparable to those of series 2 (table 4). The explanation is probably that the driving force for hydrate formation is small in the beginning of the series 3 experiments and the conditions of the experiments resemble those of series 2 at later stages. In series 3 the standard deviation on the amount of hydrates formed is higher compared to the previous series, indicating that impurities in some way make the growth rate more random.

One can also observe that the average $A * k$ gets smaller as more hydrates are formed. This is most likely due to the reduction of the interfacial area caused by formation of a hydrate slurry layer between the two fluid phases.

CONCLUSIONS

Reproducing induction times in "clean" laboratory conditions seems very difficult if not impossible. Deliberate addition of impurities to the system seems to eliminate the induction time. Extreme caution should therefore be taken when operating a multiphase pipeline under conditions favourable for hydrate formation. Kinetic inhibitors that supposedly prolong the induction time should be evaluated also in the presence of considerable amounts of impurities.

The experiments reveal that the growth rate depend on the driving force. This may either be interpreted as a pressure dependence of the parameter k in the model by Skovborg or it may indicate that the building up of crystals is also a significant kinetic step. From the present experiments it is not possible to say which explanation is correct.

When analysing kinetic experiments one should consider that the system investigated may not be in thermal equilibrium at all times.

ACKNOWLEDGMENT

REFERENCES

(1)   Skyum L., 1995, "Hydrate Kinetics", M.Sc. Thesis, Department of Chemical Engineering, The Technical University of Denmark.

(2)   Andersen B.D., 1995, "Formation of Gas Hydrates", M.Sc. Thesis, Department of Chemical Engineering, The Technical University of Denmark.

(3)   Skovborg P. and Rasmussen P., 1994, "A Mass Transport Limited Model for the Growth of Methane and Ethane Gas Hydrates", Chem. Eng. Sci., **49**, 1131-1142.

(4)   Munck J., Skjold-Jørgensen S. and Rasmussen P.,1988, "Computations of the Formation of Gas Hydrates", Chem. Eng. Sci., **43**, 2661-2672.

Series 1 Experiment No.	Induction time /s	Moles of hydrate formed in 600 s.	Moles of hydrate formed in 3600 s.
M6	38209	0.0247	0.0804
M7	41827	0.0229	0.0792
M8	60066	0.0205	0.0768
M9	45509	0.0245	0.0802
M10	155361	0.0222	0.0786
M12	104444	0.0230	0.0797
M13	298416	0.0134	0.0631
M14	341430	0.0216	0.0785
M16	106390	0.0233	0.0804
M17	117085	0.0243	0.0807
M18	77961	0.0188	0.0733

Table 1. Results of series 1. T = 3 °C. Hydrate formation starts at 14 bar.

Series 2 Experiment No.	Induction time/s	Moles of hydrate formed in 600 s.	Moles of hydrate formed in 3600 s.
M20	38489	0.0294	0.1112
M21	147025	0.0262	0.1097
M22	67392	0.0275	0.1003
M23	122524	0.0313	0.1139
M24	47379	0.0222	0.1027
M25	10096	0.0269	0.0960

Table 2. Results of series 2. Thoroughly cleaned cell. T≈3 °C. Hydrate formation starts at 21 bar.

Series 3 Experiment No.	Observed Induction time/s	Time for favourable hydrate conditions /s.	Moles of hydrate formed in 600 s.	Moles of hydrate formed in 3600 s.
M30	280	285	0.0183	0.0892
M31	239	290	0.0148	0.0822
M32	229	230	0.0248	0.1038
M33	174	205	0.0193	0.0990
M34	227	235	0.0168	0.0778
M35	220	215	0.0243	0.01095
M36	233	185	0.0239	0.01029

Table 3. Results of series 3. Initial conditions similar to those of series 2.

	Moles of hydrate formed in 600 s.	Moles of hydrate formed in 3600 s.	Induction time/s
Series 1 Average	0.0217	0.0774	126063
Series 1 Standard dev.	15.2%	6.7%	81.6%
Series 1 Average k*A cm³/s	0.40	0.31	-
Series 2 Average	0.0273	0.1056	72151
Series 2 Standard dev.	11.3%	6.6%	72.7%
Series 2 Average k*A cm³	0.22	0.17	-
Series 3 Average	0.0203	0.0949	-
Series 3 Standard dev.	19.8%	12.6%	-
Series 3 Average k*A cm³	0.26	0.17	-

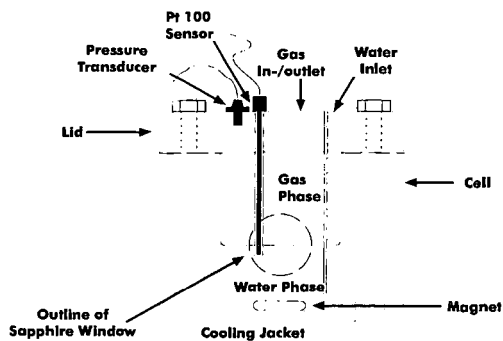Table 4. Key results of the three measurements series.
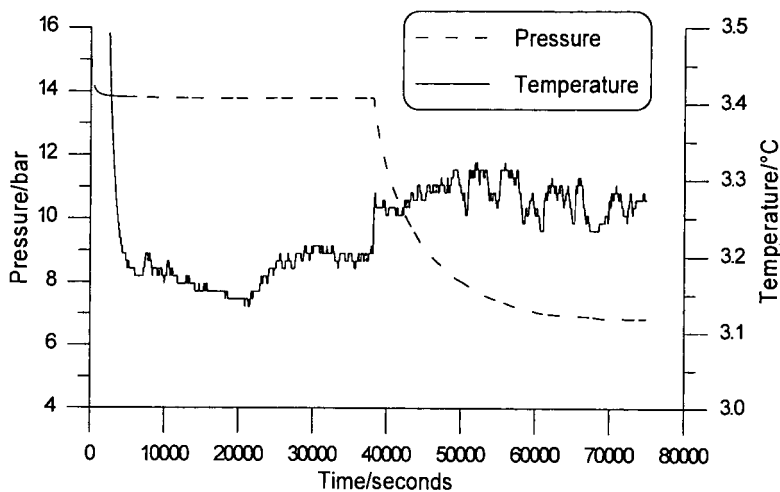
Figure 1. The Experimental Apparatus.

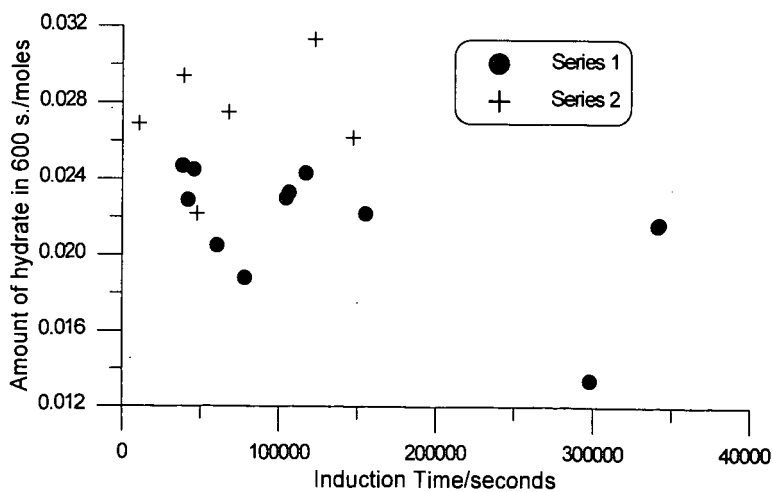**Figure 2.** Pressure and temperature vs. time in a typical experiment (M6).

Figure 3. Growth rate vs. induction time for series 1 and 2.